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LOW-FIRED PORCELAIN WITH DIOPSIDE AND MARSHALITE ADDITIONS

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The sintering, structure and properties of low-fired porcelain obtained from pastes with marshalite or marshalite with diopside replacing quartz sand are studied. The sintering temperature of porcelain made using the experimental pastes is 100°C lower (1150°C compared with 1260°C for the initial paste).

Key words: porcelain, ceramic paste, diopside, marshalite, sintering, water absorption, strength.

Research performed in the Department of Silicate and Nanomaterials Technology at Tomsk Polytechnical University on the use of diopside raw material in ceramic pastes shows that sintering of ceramic pastes obtained with diopside-containing raw material is due to the interaction with clayey components before the appearance of melt [1 – 3]. The diopside rocks in porcelain pastes are effective at contents from 5 to 15%[4] [4, 5]. The ceramic firing temperature decreases by 50°C. G. N. Maslennikova has shown than the dispersity of the silica component (quartz) has a strong effect on the sintering of porcelain and the formation of mullite [6 – 8]. It is of interest to lower the sintering temperature of porcelain pastes when using a fine, naturally occurring, crystalline silica component — marshalite.

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[4] Here and below, the content by weight, %.

The objective of the present work is to obtain and study porcelain pastes sintering at temperatures below 1200°C using marshalite and marshalite combined with diopside.

To reach this goal soft porcelain with sintering temperature 1250°C was taken at the initial material. The components of the porcelain paste are Prosyanovskoe kaolin, Veselovskoe clay, Glukhovetskoe quartz, Chupinskoe feldspar and an alumina additive.

A low sintering temperature for this porcelain (1250°C) is obtained by using Chupinskoe feldspar ($K_2O + Na_2O$ — 16.6%) and Veselovskoe clay. The chemical composition of the components is presented in Table 1.

The components activating sintering are marshalite from the Elbashinskoe deposit (Novosibirsk Oblast’) and diopside concentrates from the Burutuiskoe deposit (Irkutsk Oblast’, Southern Baikal region).

Marshalite with 93% SiO_2 is characterized by high dispersity with the 16 ìm fraction comprising 90.3%. To evaluate the effect of the active silica in the porcelain paste (paste P) the quartz sand was replaced with marshalite

TABLE 1. Chemical Composition of the Raw Material Components Used

Component	Content, wt.%								
	SiO_2	TiO	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Δm_{other}
Prosyanovskoe kaolin	47.35	0.52	37.50	0.25	0.06	0.25	0.06	0.38	13.00
Veselovskoe clay	53.70	1.25	31.26	0.73	0.92	1.04	0.42	1.88	9.20
Quartz sand	91.30	0.29	5.89	0.14	0.42	–	0.10	0.20	1.61
Chupinskoe feldspar	65.94	0.10	15.80	0.16	0.80	0.22	3.10	13.50	0.38
Dioxide concentrate	56.51	0.07	0.99	0.65	25.94	15.84	0.10	0.14	0.60
Marshalite	93.00	–	6.80	0.20	–	–	–	–	–

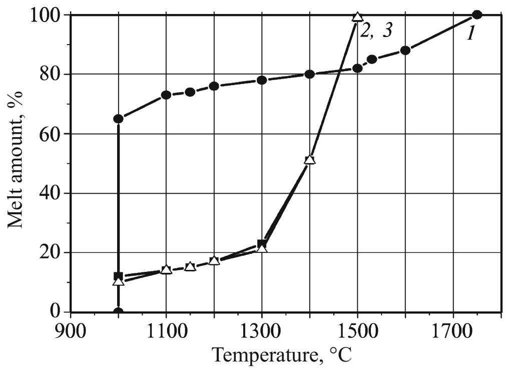

Fig. 1. Melting curves for porcelain pastes: *1*) initial paste (P); *2*) paste with diopside (PD); *3*) paste with diopside and marshalite (PDM).

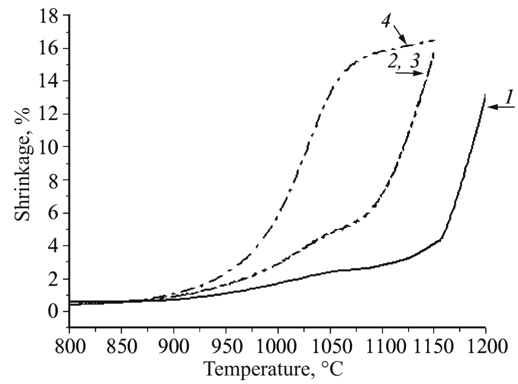

Fig. 2. Variation of the shrinkage of porcelain samples after firing at temperatures to 1200°C: *1*) initial paste (P); *2*) paste with marshalite (PM); *3*) paste with diospide concentrate (PD); *4*) paste with diopside concentrate and marshalite (PDM).

(pastes P and M, Table 2). Adequate experience in using diopside ($CaMgSi_2O_6$) has now been accumulated [1 – 3]. Diopside rocks from the Southern Baikal region are distinguished by high purity with respect to iron oxides and other coloring impurities [1].

Diopside rocks were studied both for obtaining high-quality ceramics and as a component of fine construction ceramic. Work has now begun on the diopside production in the Slyudnyanskaya group of deposits, specifically, Burtuiskoe deposit. Rocks from this deposit containing iron oxide in amounts from 2.0% in the surface layer to thousandths of percents in the main massif. Diopside concentrate was obtained from an intermediate layer, where the Fe_2O content is 0.65%.

The initial porcelain paste contains 28% quartz sand (paste P, Table 2). The effect of diospide on the sintering of porcelain was evaluated in pastes with 10% diopside content with partial replacement of quartz sand (8%) and exclusion of alumina (paste PD). In the porcelain paste PDM the quartz sand (28%) and alumina (2%) were completely replaced with a diopside concentrate (10%) and marshalite (20%).

Analysis of the melting curves for the experimental ceramic pastes in the system $K_2O–Al_2O_3–SiO_2$ (Fig. 1) shows that the initial porcelain paste is characterized by a large quantity of the primary melt (about 66%) at 1000°C with an even increase to 100% to temperature 1750°C. This shows that sintering of articles made from this paste is characterized by a narrow temperature interval of the sintered state, as actually observed in practice. At sintering temperatures below 1250°C the article are underfired and 10 – 15°C above 1250°C they become deformed. The melting curves for porcelain paste with marshalite are similar to those for the initial paste.

The character of the melting curve changes considerable when diopside is introduced into the paste in the amount 10%. The melting curve for the pastes (with diopside and with diopside introduced concurrently with marshalite) is characterized by a small amount of primary melt (about 10%). The melt increases to 50% in the temperature interval from 1000 to 1400°C. Complete melting of the PD and PDM porcelain is attained at 1520°C, which is lower than for the primary paste (it melts completely at 1750°C). The character of the melting curve (PD and PDM pastes) predicts a wider interval of sintering and the sintered state of ceramic pastes with diopside and diopside and marshalite.

We shall examine the experimental results on the sintering of porcelain pastes with plastic formation of articles.

A comparative analysis of the shrinkage curves obtained while firing samples of the experimental pastes (PM, PD, pMD) shows (Fig. 2) that the total shrinkage of samples of these pastes is the same and equals 16.5%, while for samples of the initial paste (P) such shrinkage is reached only at 1250°C. Intense shrinkage of the initial paste starts at 1120°C. When quartz is replaced with marshalite in the ceramic paste (PM) the analogous shrinkage starts at 980°C, i.e. by 140°C lower. Such a change of shrinkage is observed when 10% diopside is introduced instead of alumina (2%) and quartz (8%) (paste PD). For these porcelain pastes shrinkage occurs in two temperature intervals. The first one (100 – 1070°C) is related with the sintering of alumina components (shrinkage to 5%) while the second temperature in-

TABLE 2. Components of Porcelain Pastes

Components	Weight content, %			
	P	PM	PD	PDM*
Prosyanovskoe kaolin	36	36	36	36
Veselovskoe clay	14	14	14	14
Glukhovetskoe quartz	28	–	20	–
Chupinskoe feldspar	20	20	20	20
Alumina	2	2	–	–
Diopside concentrates	–	–	10	10
Marshalite	–	28	–	20

* P) initial; PM) with marshalite; PD) with diopside; PDM) with diopside and marshalite.

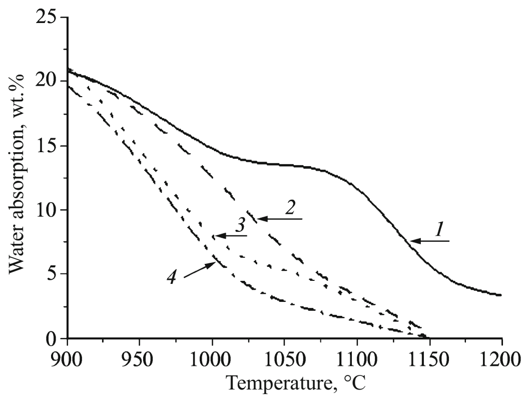

Fig. 3. Variation of water absorption of porcelain samples after firing at different temperature to 1200°C: *1 – 4*) same as in Fig. 2.

terval (1070 – 1170°C) is related with melt formation (shrinkage to 16.5%). When marshalite and diopside are introduced concurrently into the porcelain paste in the amounts 20% and 10%, respectively, as replacements for quartz sand and alumina intense sintering to 16.5% occurs in a single stage in the temperature interval 950 – 1050°C. Thus, the replacement of quartz by marshalite in the experimental porcelain paste intensifies sintering similarly to the introduction of 10% diopside. The concurrent introduction of marshalite and diopside as substitutes for quartz and alumina (data according to shrinkage and water absorption curves) lowers the sintering temperature by more than 100°C.

Analysis of the variation of the water absorption of the samples as a function of the firing temperature (Fig. 3) shows for firing of the initial paste zero water absorption is not attained even at 1200°C (2.2%). The samples of the porcelain pastes with diopside reach zero water absorption at temperature 1150°C. For firing of samples of porcelain pastes with diopside and marshalite at 1100°C water absorption approaches zero (1.0 – 1.5%), which corresponds to semi-porcelain; zero water absorption is attained at 1120°C.

In summary, when diopside concentrate is used in the amount 10% and marshalite is substituted for quartz sand (20%) the sintering temperature of the porcelain pastes decreases by 100 – 150°C compared with the initial paste. The study of the sintering of porcelain pastes confirmed that the introduction of fine silica (marshalite) decreases the sintering temperature of porcelain. And, the firing temperature decreases from 1250 to 1150 – 1170°C. The results confirmed that the introduction of diopside (paste PD) lowers the firing temperature of porcelain by 100°C. When diopside and marshalite are introduced concurrently the sintering temperature of porcelain decreases to 1120°C.

The properties of porcelain after firing to zero water absorption are presented in Table 3.

The paste containing marshalite with diopside (PDM) sinters at 1120 – 1150°C, and articles are characterized by high strength. The paste composition has have been patented [10].

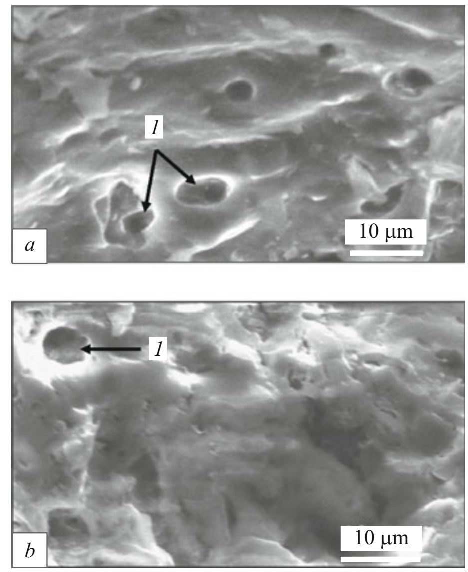

Fig. 4. Electron-microscopic photographs of porcelain obtained with the initial paste (P): *a*) firing temperature 1250°C; *b*) firing temperature 1150°C; *1*) quartz grain.

Photomicrographs obtained with a scanning electron microscope from a cleavage surface of porcelain obtained with the primary paste (Fig. 4) show grains after firing at 1250°C and after firing as 1150°C (water absorption 4%). Quartz grains are not seen in electron microscopic photographs of porcelain with marshalite after firing at 1150°C (Fig. 5*a*). Quartz grains are seen in a photograph of porcelain with diopside (Fig. 5*b*), since the paste contains 20% quartz sand.

Distinct crystals of quartz and other crystalline phases are not seen in the electron-microscopic photograph of a cleavage surface of porcelain from PDM paste containing diopside and marshalite (Fig. 6). However, they are recorded by x-ray methods (Fig. 7). Diffraction peaks corresponding to quartz, diopside and a mullite-like aluminum-silicate phase are seen in the x-ray diffraction pattern of porcelain from paste with diopside and marshalite.

The results of this work show that introducing marshalite and diopside concurrently into the paste for low-temperature porcelain lowers the sintering temperature to zero water ab-

TABLE 3. Firing Temperature and Properties of Porcelain Articles made with the New Pastes

Indicator	Post-sintering samples from the experimental pastes			
	P	PM	PD	PDM
Temperature, °C	1260 ± 10	1170 – 1200	1150 – 1170	1120 – 1150
Water absorption, %	0.0	0.0	0.0	0.0
Compression strength, MPa	22.0	35.0	39.0	39.5
Shrinkage, %	16.2	15.6	15.7	16.51

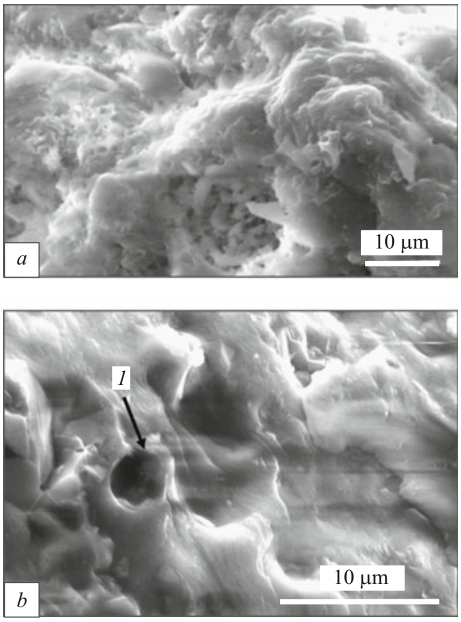

Fig. 5. Electron-microscopic photographs of cleavage face of porcelain after firing at 1150°C: *a*) paste with marshalite (PM); *b*) paste with diopside concentrate (PD); *1*) quartz grain.

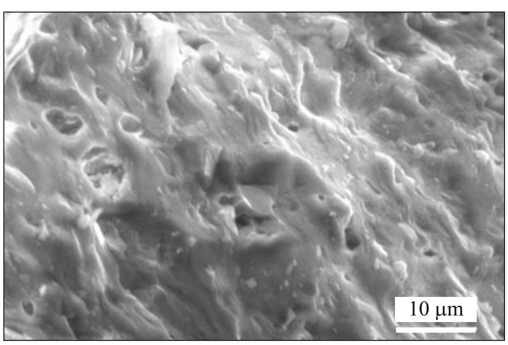

Fig. 6. Electron-microscopic photograph of a cleavage surface of ceramic with paste containing diopside and marshalite (PDM), fired at 1150°C.

sorption by 100 – 120°C and expands the interval of the sintered state from 20 to 100°C.

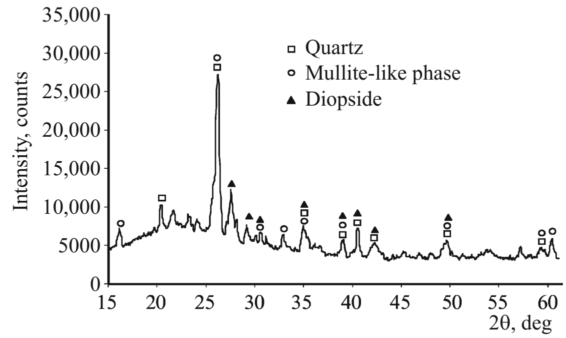

Fig. 7. X-ray diffraction pattern of porcelain obtained with paste containing diopside and marshalite (PDM) after firing at 1150°C.

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